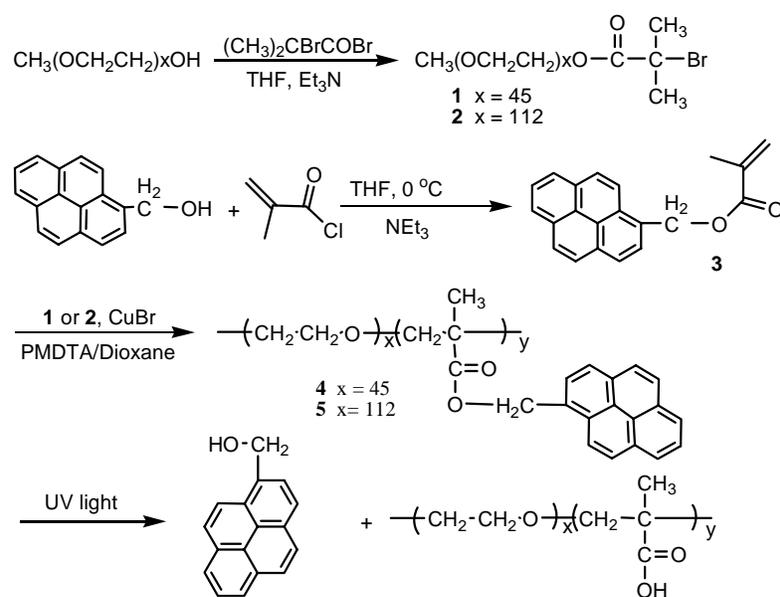


Supporting Information

A New Design for Light-Breakable Polymer Micelles

1. Synthesis and Characterization of Diblock Copolymer

Materials. Dioxane and THF were purified by distillation from sodium with benzophenone. Catalyst Cu(I)Br was washed repeatedly with acetic acid and ether, then dried and stored under nitrogen. 2-Bromo-2-methylpropionyl bromide, methacryloyl chloride, 1-pyrenemethanol, N, N, N', N''-pentamethyldiethylenetriamine (PMDTA) and triethylamine were purchased from Aldrich and used without further purification. Poly(ethylene glycol) methyl ether with number-average molecular weight about 2000 and 5000 g mol⁻¹ (from Aldrich) were used to prepare poly(ethylene oxide) (PEO) macroinitiators.



Scheme 1. Synthetic route to diblock copolymer and its photo-solvolysis

Synthesis of PEO Macroinitiators (1 and 2).¹ As an example, a solution of 1.8 g (7.7 mmol) of 2-bromo-2-methylpropionyl bromide in 10 ml of dry THF was added to a mixture of 1.1 g (10 mmol) of triethylamine and 10 g (5 mmol) of P(ethylene glycol) methyl ether with an *M_n* of 2000 in 30 ml of THF at 0 °C. The mixture was stirred for 18 h. After the mixture was filtered, half of the solvent was evaporated, and the PEG macroinitiator was precipitated into cold ether. After dissolution in ethanol, the solution was stored in refrigerator to precipitate the product. Yield: 70%.

¹H NMR (CDCl₃), δ (ppm): 4.33 (dd, 2 H, -OCH₂COO-), 3.73 (m, 158H, -CH₂-), 3.38 (s, 3H, -OCH₃), 1.94 (s, 6H, (CH₃)₂CBrCOO-). Mw/Mn = 1.11 (GPC using polystyrene standards).

Synthesis of Pyrene-containing Methacrylate Monomer (3): (1-Pyrene)methyl 2-methyl-2-propenonate.²

1-Pyrenemethanol (5 g; 0.022 mol) was added to a solution of triethylamine (9.0 mL; 0.065 mol) in 250 mL of anhydrous THF. Methacryloyl chloride (6.3 mL; 0.065 mol) was added dropwise under stir at 0 °C. The reaction was then conducted at room temperature overnight. The reaction medium was filtered.

The solvent was evaporated, and the solid residue has been purified by recrystallization in 95% ethanol at 40 °C (yield = 90%). MS (m/e): 300 (M⁺). ¹H NMR (CDCl₃), δ ppm: 7.99-8.19 (m, 9H, aromatic H), 6.15 (s, 1H, CH₂=C), 5.89 (s, 2H, CH₂O), 5.56 (s, 1H, CH₂=C), 1.97 (s, 3H, CH₃).

Synthesis of Pyrene-Containing Diblock Copolymers (4 and 5). As an example, Cu(I)Br (10.6 mg, 0.074 mmol), macroinitiator **1** (74 mg, 0.037 mmol) and monomer **3** (1 g, 3.33 mmol) were mixed in a 5 mL ampoule, degassed, and filled with nitrogen. Then, PMDTA (13 mg, 0.074 mmol) dissolved in dioxane (3 mL) was added through a syringe. The mixture was degassed three times using the freeze-pump-thaw procedure and sealed under vacuum. After 30 min stirring at room temperature, the ampoule was placed in a preheated oil bath (90 °C) for 14 h. The solution was passed through a neutral Al₂O₃ column with THF as eluent to remove the catalyst. The light yellow filtrate was concentrated under reduced pressure and reprecipitated twice into methanol and washed with hexane. The diblock copolymer was collected by filtration and dried under vacuum. Yield: 60 %. M_n (NMR) = 23,500; M_w/M_n=1.38 (GPC). This sample is denoted as PEO₄₅-*b*-PPy₇₂, where the two numbers indicate the numbers of EO and Py units respectively. Other samples prepared include PEO₄₅-*b*-PPy₄₅ (M_w/M_n=1.20) and PEO₁₁₂-*b*-PPy₅₅ (M_w/M_n=1.18). The results shown in the paper were obtained with PEO₄₅-*b*-PPy₇₂.

Characterizations. ¹H NMR spectra were obtained with a Bruker Spectrometer (300 MHz, AC 300). UV-vis spectra were recorded on a Hewlett-Packard 8452A diode array spectrophotometer. Gel permeation chromatography (GPC) measurements were performed using a Waters system equipped with a refractive index and a photodiode array detector; THF being used as eluent (elution rate, 0.5 mL/min) and polystyrene standards used for calibration. Fluorescence emission spectra were recorded on a SPEX 1680 Double-Monochromator spectrometer. An optical setup was utilized to monitor the process of UV light-induced dissociation of micelles in situ. In these experiments, the micellar solution (~ 3 mL) was filled in a standard quartz cuvet (1cm × 1 cm cross section) with mild stir, the change in optical transmittance of the solution, while under UV light irradiation, was measured at 633 nm (He-Ne laser, far from absorption of pyrene) using a high-speed photodetector (Displaytech) collected to a digital oscilloscope (Tektronix, TDS 420A). The irradiation light, obtained from a UV-vis spot curing system (Novacure) combined with a 365 nm filter, was applied vertically from above the tube. Micellar aggregates were examined using a Hitachi H-7500 transmission electron microscope (TEM) operating at 80 KV and a Hitachi S-4700 Field Emission Gun scanning electron microscope (SEM) operating at 3 KV. To prepare samples for SEM or TEM observations, typically one drop of diluted micellar solution was cast on either silicon wafer (for SEM) or carbon-coated copper grid (for TEM), and dried at room temperature.

2. UV-Vis and Fluorescence Spectra

Figure 1 shows UV-vis spectra of PEO-*b*-PPy and the hydrophobic dye of Nile Red in THF. The characteristic absorption bands of pyrene above 300 nm can be seen from the spectrum of the diblock copolymer. In contrast, Nile Red has no absorptions in the range of 340-400 nm, its maximum absorption is centered at ~ 540 nm. Figure 2 shows fluorescence emission spectra of a micellar solution (with no Nile Red) before and after UV light irradiation. In this case, PEO-*b*-PPy micelles were obtained by adding 15 wt% of water in a THF solution (initial polymer concentration 0.25 mg mL⁻¹) with stir. By exciting at 375 nm, the micellar solution displays only the excimer emission of pyrene peaked at about 478 nm. For comparison, the spectrum of PEO-*b*-PPy in THF alone is also shown. It is

seen that even for well-dissolved block copolymer without micelle formation, the high concentration of pyrene moieties on the polymer gives rise to the excimer emission only. Now, after 10 min UV light exposure of the micellar solution (in this example, 5000 mW applied to 3 mL solution), the monomer emissions at lower wavelengths (~ 380-410 nm) become dominant. As the UV irradiation time increases, the intensity of monomer emission rises at the expense of excimer emission. These results clearly confirm the occurrence of the photo-solvolysis of pendant pyrene groups on the PPy block and the resultant detachment of pyrene moieties from the polymer (Scheme 1). Since cleaved pyrenemethanol molecules are soluble in the mixture of THF/water (15 wt%), the monomer fluorescence emission can be observed. When this experiment of UV light-induced micelle breaking was conducted on PEO-*b*-PPy micelles soluble in water (after evaporation of THF), the drastic reduction of excimer emission took place after UV irradiation, but no significant monomer emission was observed because detached pyrenemethanol precipitated in water. In this case, the time of photo-solvolysis of pendant pyrene groups, which determines the irradiation time required for micelle dissociation, was also found to be longer than in THF/water solution. This is understandable because when PEO-*b*-PPy micelles are diluted in water, the quenching effect solidifies the compact PPy cores, which would slow down the speed of photo-solvolysis

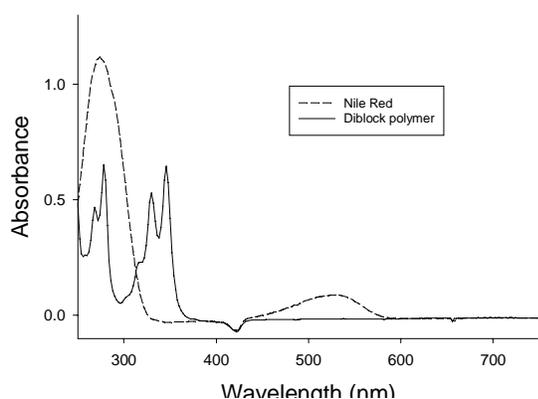


Figure 1. UV-vis spectra of PEO-*b*-PPy diblock copolymer and Nile Red in THF.

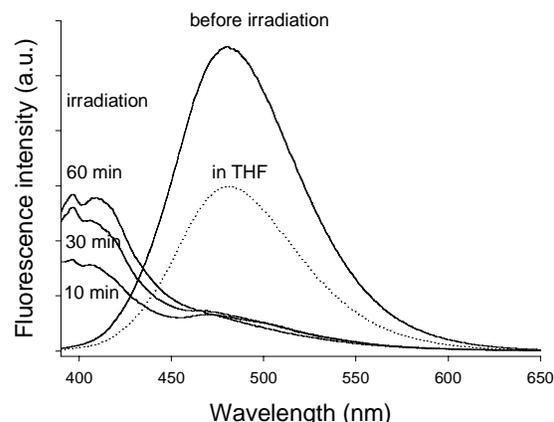


Figure 2. Fluorescence emission spectra ($\lambda_{\text{ex}}=275$ nm) of PEO-*b*-PPy diblock copolymer in THF, its micellar solution in THF/water (15 wt%) before and after UV light irradiation for different times.

3. NMR Measurements

As shown in Figure 3, the detachment of 1-pyrenemethanol from the polymer under UV irradiation was also confirmed by ^1H NMR measurement. In this experiment, in order to better observe the spectral changes, the micellar aggregate solution was prepared using a higher polymer concentration of 1.0 mg/mL in THF followed by adding about 10% of water (deuterated solvents). For comparison, the diblock copolymer dissolved in THF is also shown. The used UV irradiation intensity was 3000 mW. From the peak assignment, it is seen that 1-pyrenemethanol was formed after 1 min irradiation, and its amount increased with the irradiation time. The degree of photo-solvolysis (in percentage) estimated from the NMR spectra was indicated in the figure.

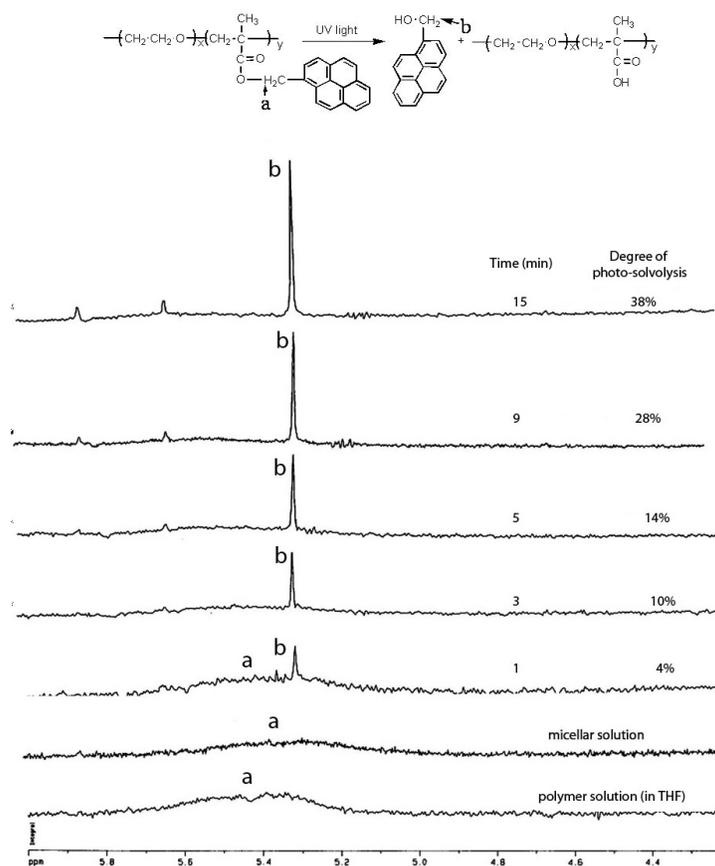


Figure 3. ^1H NMR spectra of a micellar solution of PEO-*b*-PPy under UV irradiation, showing increase in the amount of detached 1-pyrenemethanol.

4. GPC Measurements

GPC measurements were carried out to see if the ester group linking the PEO and PPy blocks (scheme 1) could also be broken by UV irradiation. Without ruling out the possibility, especially at high irradiation intensities with long exposure times, no significant cleavage was observed under the used experimental conditions. The example of GPC curves in Figure 4 shows that after 20 min irradiation on a THF solution of the diblock polymer using a high UV intensity of 3000 mW, the peak displayed no changes. The breaking of this ester group would result in a shift of the peak to higher retention times. We were unable to do the analysis with ^1H NMR due to the too small concentration of the linking ester group.

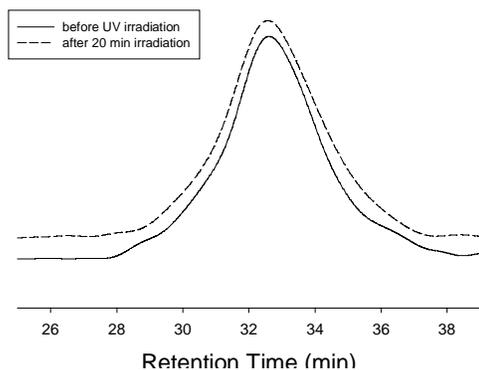


Figure 4. GPC curves of PEO-*b*-PPy diblock copolymer in THF before and after 20 min UV irradiation (3000 mW).

5. TEM Observations

TEM observations also found clear dissociation of PEO-*b*-PPy micelles in solution under UV light irradiation. The example of TEM images in Figure 5 shows the dissociation of micellar aggregates with encapsulated Nile Red. In this case, PEO-*b*-PPy and Nile Red were dissolved in THF (polymer concentration, 0.725 mg/mL; 6 wt% Nile Red with respect to the amount of polymer); then ~ 17 wt% of water was added dropwise to induce the micellar aggregation and the solubilization of Nile Red by hydrophobic PPy cores. The micellar solution was diluted by 4-fold volume of water, and THF was removed by evaporation at 40 °C. For TEM observation, a drop of this solution was cast on a copper grid and dried. About 5 mL of the same solution was placed in a small bottle and exposed to UV light (2000 mW) for 45 min before the solution was cast and dried. It is seen that the micellar solution contains micellar aggregates (vesicles and larger capsule-like aggregates) before irradiation, and that the micellar aggregates were disappeared after irradiation. The change under UV irradiation could be observed visually. The initially translucent micellar solution became quite opaque due to detached pyrenemethanol and released Nile Red molecules that are both insoluble in water. Please note that the initial polymer concentration used in this experiment (0.725 mg/mL) was much higher than that (0.25 mg/mL) used to prepare the core-shell micelles shown in Figure 2 in the paper. For a same amphiphilic block copolymer, the morphology and size of its micellar aggregates depend upon a number of parameters that include the initial polymer concentration (larger aggregates would be expected at higher polymer concentration). Indeed, the mechanism of dissociation designed in this study ensures that all micellar aggregates formed by PEO-*b*-PPy can be dissociated by UV light irradiation.

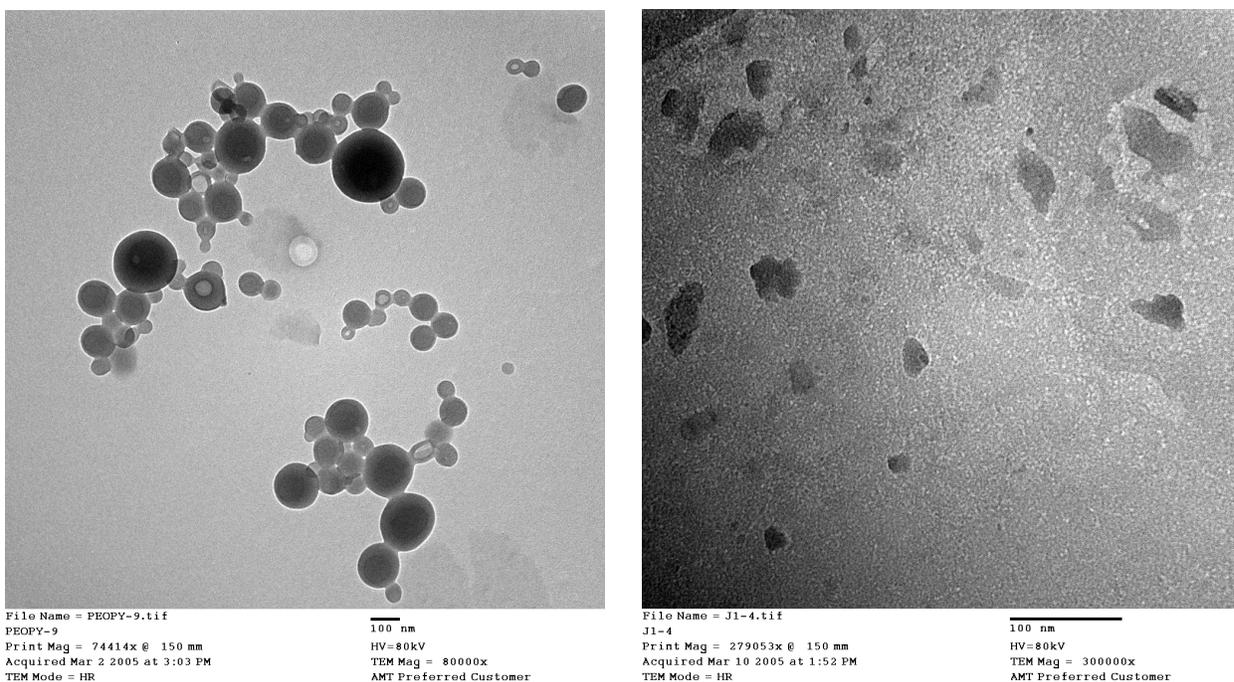


Figure 5. TEM images showing micellar aggregates of PEO-*b*-PPy with encapsulated Nile Red (left) and their dissociation after the micellar solution was exposed to UV light (right).

References

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2. Lou, X.-D.; Daussin, R.; Cuenot, S.; Duwez, A.-S.; Pagnouille, C.; Detrembleur, C.; Bailly, C.; Jérôme, R. *Chem. Mater.* **2004**, *16*, 4005.